



Patent
Attorney Docket No. 003301-053

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

MIKHAIL KEJZELMAN et al.

Group Art Unit: 1742

Application No.: 10/743,094

Examiner: Unassigned

Filing Date: December 23, 2003

Confirmation No.: 8005

Title: IRON-BASED POWDER

SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

The benefit of the filing date of the following priority foreign application(s) in the following foreign country is hereby requested, and the right of priority provided in 35 U.S.C. § 119 is hereby claimed.

Country: Sweden

Patent Application No(s).: 0203851-1

Filed: December 23, 2002

In support of this claim, enclosed is a certified copy(ies) of said foreign application(s). Said prior foreign application(s) is referred to in the oath or declaration. Acknowledgment of receipt of the certified copy(ies) is requested.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By



Benton S. Duffett, Jr.

Registration No. 22,030

P.O. Box 1404
Alexandria, Virginia 22313-1404
(703) 836-6620

Date: April 9, 2004

BURNS DOANE

BURNS DOANE SWECKER & MATHIS LLP
INTELLECTUAL PROPERTY LAW

SUBMISSION OF CERTIFIED COPY
OF PRIORITY DOCUMENT

(02/04)

PRV

PATENT- OCH REGISTRERINGSVERKET
Patentavdelningen



Intyg Certificate

Härmed intygas att bifogade kopior överensstämmer med de handlingar som ursprungligen ingivits till Patent- och registreringsverket i nedannämnda ansökan.

This is to certify that the annexed is a true copy of the documents as originally filed with the Patent- and Registration Office in connection with the following patent application.

(71) Sökande Höganäs AB, Höganäs SE
Applicant (s)

(21) Patentansökningsnummer 0203851-1
Patent application number

(86) Ingivningsdatum 2002-12-23
Date of filing

Stockholm, 2004-01-19

För Patent- och registreringsverket
For the Patent- and Registration Office

Hjördis Segerlund
Hjördis Segerlund

Avgift
Fee 170:-

IRON-BASED POWDER

Field of the invention

The present invention relates to new metal powder compositions. More specifically, the invention concerns a new iron-based powder which is useful for the preparation of soft magnetic materials having improved properties when used both at high and low frequencies. The invention also concerns a method for the manufacturing of soft magnetic composite materials prepared therefrom.

Background of the invention

Soft magnetic materials are used for applications, such as core materials in inductors, stators and rotors for electrical machines, actuators, sensors and transformer cores. Traditionally, soft magnetic cores, such as rotors and stators in electric machines, are made of stacked steel laminates. Soft Magnetic Composite, SMC, materials are based on soft magnetic particles, usually iron-based, with an electrically insulating coating on each particle. By compacting the insulated particles optionally together with lubricants and/or binders using the traditionally powder metallurgy process, the SMC parts are obtained. By using this powder metallurgical technique it is possible to produce materials having a higher degree of freedom in the design of the SMC component than by using the steel laminates as the SMC material can carry a three dimensional magnetic flux and as three dimensional shapes can be obtained by the compaction process.

Two key characteristics of an iron core component are its magnetic permeability and core loss characteristics. The magnetic permeability of a material is an indication of its ability to become magnetised or its ability to carry a magnetic flux. Permeability is defined as the ratio of the induced magnetic flux to the magnetising force or field intensity. When a magnetic material is exposed to a varying field, energy losses occur due to both hysteresis losses and eddy current losses. The hysteresis loss is brought about by the necessary expenditure of energy to overcome the retained magnetic forces within the iron core component. The eddy current loss is brought about by the production of electric currents in the iron core component due to the changing flux caused by alternating current (AC) conditions. A high electrical resistivity of the component is desirable in order to minimise the eddy currents.

Research in the powder-metallurgical manufacture of magnetic core components using coated

iron-based powders has been directed to the development of iron powder compositions that enhance certain physical and magnetic properties without detrimentally affecting other properties of the final component. Desired component properties include e.g. a high permeability through an extended frequency range, low core losses, high saturation induction, and high strength. Normally an increased density of the component enhances all of these properties. The desired powder properties include suitability for compression moulding techniques, which i.e. means that the powder can be easily moulded to a high density component, which can be easily ejected from the moulding equipment without damages on the component surface.

A large number of patent publications teach different types of electrically insulating coatings. Examples of recently published patents concerning inorganic coatings are the US patents 6309748 and US 6348265. The US 6309748 concerns ferromagnetic particles having a coating including from 2 to 4 parts of an oxide and one part of a chromate, molybdate, oxalate, phosphate, or tungstate and the US 6348265 concerns particles of a base powder consisting of essentially pure iron having an insulating oxygen- and phosphorus-containing barrier.

Coatings of organic materials are known from e.g. the US patent 5595609, which discloses magnetic powder the particles of which are encapsulated with a thermoplastic coating selected from the group of polybenzimidazole and polyimides having heat deflection temperatures of at least about 400 °C.

Coatings comprising both inorganic and organic material are known from e.g. the US patent 6372348 according to which an annealable insulating material has at least one inorganic compound and at least one organic polymeric resin. Another publication disclosing coatings of both inorganic and organic material is the US patent 5 063 011, according to which publication the particles are surrounded by an iron phosphate layer and a thermoplastic material.

In these known methods one of the reasons for applying a second coating consisting of an organic material, such as thermoplastics or polymeric resins, is to increase the strength of the component. It is then necessary that the organic material does not decompose when the component is heat treated after the compaction. The method according to the present invention distinguishes from the prior art methods i.a. in that according to the present

invention it is possible to prepare compacts having high densities and good magnetic properties, which compacts also after heat treatment to temperatures above the decomposition temperature of the organic material have high strength.

Summary of the invention

The present invention concerns an improvement of a ferromagnetic powder having particles with an electrically insulation surrounding the particles. More specifically the present invention concerns a ferromagnetic powder having coarse, soft magnetic, electrically insulated iron or iron-based particles, the surfaces of which are modified. The invention also concerns a method of preparing such particles and a method of preparing high density, soft magnetic composite materials by uniaxially compacting the new powder in a die at high pressure.

Detailed description of the invention

The ferromagnetic powders used herein are made up of iron or an alloy containing iron optionally in combination with up to 20 % by weight of one or more of element selected from the group consisting of aluminium, silicon, chromium, niobium, molybdenum, nickel and cobalt. Preferably the new powder is based on a base powder which consists of essentially pure iron. This powder could be e.g. a commercially available water-atomised, a gas-atomised iron powder or a sponge iron powder with round, irregular or flat particles.

Preferred electrically insulating coatings which may be used according to the invention are thin phosphorous containing coatings of the type described in the US patent 6348265 which is hereby incorporated by reference. Also other, preferably inorganic coatings may be used, for example coatings based on Cr, Mg or Mo.

An important feature of the invention is that the powder used have coarse particles i.e. the powder is essentially without fine particles. The term "essentially without fine particles" is intended to mean that less than about 5 % of the powder particles have a size below 45 µm as measured by the method described in SS-EN 24 497. So far the most interesting results have been achieved with powders essentially consisting of particles above about 106 µm and particularly above about 212 µm. The term "essentially consisting" is intended to mean that at least 10 % preferably at least 40 % most preferably at least 60 % of the particles have a particle size above 106 and 212µm respectively. So far the best results have been obtained

with powders having a particle size above about 212 μm . The maximum particle size may be about 5 mm.

It is known that the particle size can be selected according to the frequency band required and that powders having coarse particles are used for the manufacture of soft magnetic components. Thus the US patent 6309748 discloses a ferromagnetic powder, the particles of which have a diameter size between 40 and 600 μm . In contrast to the iron or iron based powder particles according to the present invention, these powder particles are not surface modified. In the US patent 4190441 a powder composition for production of sintered soft magnetic components is disclosed. In this patent the iron powder includes particles with less than 5% exceeding 417 μm and less than about 20 % of the power particles have a size less than 147 μm . This powder is mixed with specific amounts of ferrophosphorus in order to obtain the soft magnetic components. These known powder particles are not provided with an insulating layer and the are not surface modified. Additionally, coarse powders for the preparation of soft magnetic components are known from the US patent 4272747. According to this patent the powder particles , which may be insulated, are selected in such a way that they pass through a 100 Tyler mesh sieve but not through a 300 Tyler mesh size sieve. Furthermore, the powder particles may be insulated but nothing is taught about surface modification and the obtained bodies have a density from 2 to 6.5 g/cm³.

A critical feature of the powder according to the present invention is that, before compaction, the particles have been treated with a surface modifying agent, which adheres to and is compatible with the insulating coating surrounding the separate powder particles. This agent may be selected from the group consisting of organo alkoxysilanes, organo silazanes, fluorine-containing silicon silane coupling agents, titanate coupling agents, Zr and Al coupling agents, fatty acids, particularly saturated and unsaturated fatty acids having 10 to 24 C atoms in the alkyl chain, e.g. stearic acid, oleic acid, fatty acid esters, such as glyceryl monostearate, fatty acid amides, particularly saturated fatty acid mono- and bisamides, such as stearic monoamide, EBS, unsaturated fatty acid mono- and bisamides, such as oleic monoamide, EBO, mixed fatty acid amides, fatty acid derivative mixtures, and metal soaps. Especially preferred are alkylalkoxy silanes wherein the alkyl group has between 10- 24 carbon atoms or fatty acids with 11-25 carbon atoms. Most preferred are hexadecyltrimethoxy silane and stearic acid. Multilayer and composite layers of the above mentioned surface-modifying agents may also be used.

Different methods may be used for the surface modifying of the iron-based powder. According to one method the surface-modifying agent can thus be dissolved or dispersed in a suitable solvent, e.g. an organic solvent, such as acetone and ethanol. The obtained solution or dispersion is subsequently added to the iron based powder during mixing and optionally heating. The solvent is finally evaporated optionally in vacuum. Alternatively, the surface modification may be performed by melting a solid surface modifying agent, mixing the heat melted surface modifying agent with a heated iron-based powder mixture followed by cooling during mixing. Heating may of course also be applied to a premixed mixture of iron-based powder and surface modifying agent. The modifying agent may be applied by spraying. The amount of the surface-modifying agent depends on the size of particle of the iron-based powder. Normally a powder having larger particles requires less surface-modifying agent than a powder having smaller particles. At present it has been found that excellent results can be obtained with an amount of the surface-modifying agent between 0.005- 0.5 %, preferably between 0.05- 0.4 % and most preferably between 0.1- 0.3 % by weight of the insulated powder.

The powder to be compacted may also include additives selected from the group consisting of binders, lubricants and flow enhancing agents. An important feature of the invention is that no separate lubricant must be added to the composition before compaction and the high density components with good surface finish can be obtained even without die wall lubrication. The new powders according to the present invention may of course also be used in combination with internal lubrication, external lubrication or a combination of both. Examples of lubricants which may be used in addition to organic PM lubricants are inorganic lubricants such as hexagonal boron nitride, MoS₂ and graphite.

The invention also comprises a method of preparing high density soft magnetic parts. According to this method the new surface modified powder according to the present invention is optionally mixed with an additive such as a binder and/or a flow enhancing agent. A lubricant may also be added to the mix. The powder composition is subsequently uniaxially compacted, preferably in a single step, at high compaction pressure in a die. The obtained green body is ejected from the die and optionally heat treated. The compaction may be performed at ambient or elevated temperature.

The term "at high compaction pressure" is intended to mean at pressures of about at least 600 MPa. More interesting results are obtained with higher pressures such as pressures above 800, or more preferably above 1000 MPa.

Conventional compaction at high pressures, i.e. pressures above about 800 MPa with conventionally used powders are generally considered unsuitable due to the high forces required in order to eject the compacts from the die, the accompanying high wear of the die and the scratchy components obtained. By using the new powders according to the present invention it has unexpectedly been found that the high density compacts can be obtained with compaction at high pressures, about 1000 MPa, and that the components ejected from the die have acceptable or even perfect surface finishes.

The compaction may be performed with standard equipment, which means that the new method may be performed without expensive investments. The compaction is performed uniaxially and preferably in a single step at ambient or elevated temperature. Alternatively the compaction may be performed with the aid of a percussion machine (Model HYP 35-4 from Hydropulsor) as described in patent publication WO 02/38315.

The heat treatment may be performed at the temperatures normally used, e.g. up to temperatures of about 700°C in different types of atmospheres or at reduced pressure and optionally in the presence of steam.

In this context the term "high density" is intended to mean compacts having a density of at least about 7.45 g/cm³ and above. Components having lower densities can of course also be produced.

In brief the advantages obtained by using the powder according to present invention are that SMC parts having low core loss and high induction can be obtained. Other advantages are that the strength after heat treatment is increased and that, in spite of very high densities, the compacted parts can be successfully ejected from the dies without problems with negative influence on the die walls and on the surfaces of the compacted SMC parts. It is thus possible to obtain parts having excellent surface finish. These results can be obtained with a single compaction step. Examples of products for the new powder is of special interest are inductors, stators and rotors for electrical machines, actuators, sensors and transformer cores.

The invention is further illustrated by the following examples.

Example 1

An iron-based water atomised powder (Somaloy 550, available from Höganäs AB, Sweden) was used as starting material. This powder has an average particle size between 212 and 425 μm and less than 5 % of the particles have a particle size below 45 μm . This powder, which is a pure iron powder, the particles of which are electrically insulated by a thin phosphorus containing barrier, was treated with 0.2 % by weight of a hexadecyl trimethoxysilane as a surface modifying agent. The surface modifying process was performed as follows: hexadecyl trimethoxysilane was diluted in ethanol to a 20 % solution, by weight, and the solution was stirred during 60 minutes. An amount of this solution corresponding to 0.2 % by weight was added during mixing to the iron powder, which had previously been heated to 75 °C in the mixer. An intensive mixing was carried out in the same mixer during 3 minutes followed by mixing at a lower speed during 30 minutes and during vacuum in order to evaporate the solvent. A corresponding powder without surface modification was used as comparison. This powder was mixed with a lubricant, Kenuolube™ before the compaction. The amount of the lubricant used was 0.5 % of the composition, which is generally considered as a low amount of lubricant for components compacted at high pressures.

Rings with an inner diameter of 47 mm and an outer diameter of 55 mm and a height of 4 mm were uniaxially compacted in a single step at different compaction pressures 800, 1000 and 1200 MPa, respectively. Despite the low amount of surface modifying agent and relatively high compaction pressures the surfaces of the components showed no sign of deterioration.

After compaction the parts were heat treated at 500 °C for 30 minutes in air. The obtained heat treated rings were wound with 25 sense and 112 drive turns. The magnetic properties were measured in an LDJ 3500 Hysteresigraph. Table 1 summarizes the maximum relative permeability and the magnetic induction at 1500 and 6900 A/m respectively, measured under DC conditions. The core loss/cycle has also been measured at 1 T and 50 and 400 Hz.

The following table 1 demonstrates the obtained results:

Table 1

Sample	Compaction Pressure MPa	Density g/cm ³	μ_{\max}	B ₁₅₀₀ (T)	B ₆₉₀₀ (T)	Core loss/cycle at 1T and 50 Hz (J/kg)	Core loss/cycle at 1T and 400 Hz (J/kg)
According to the invention	800	7.45	720	1.08	1.53	0.134	0.178
	1000	7.59	790	1.15	1.59	0.126	0.163
	1200	7.64	820	1.18	1.62	0.124	0.165
Comparative example	800	7.39	620	0.95	1.46	0.142	0.200
	1000	7.47	590	0.95	1.49	0.140	0.198
	1200	7.49	550	0.92	1.48	0.140	0.193

As can be seen from table 1 the green density is significantly higher for the surface modified material and magnetic properties are hence improved compared with the materials used in the comparative examples, which demonstrate that no or only minor improvements of the magnetic properties can be obtained by increasing the compaction pressure to 1000 MPa and 1200 MPa.

From table 1 it can also be concluded that the density values as a function of compaction pressure is diverging when the compaction pressure is increased, extrapolation of the curves reveals that from a compaction pressure of about 600 MPa the density values for the material according to the invention will be higher compared with the density values for the comparative example.

Despite the obtained high density of the samples the core losses are maintained at a low level even at 400 Hz which shows that the electrical insulating layers are maintained.

Samples produced according to example 1 were tested with regard to transverse rupture strength after heat-treatment at 500°C for 30 minutes in air. The transverse rupture strength

was tested according to ISO 3995. Figure 1 demonstrates the transverse rupture strength at different density levels. It should be noted that, even at the same pressed density, the strength is unexpectedly higher for the surface modified material.

Example 2

A very high purity water atomised iron- based powder, the particles of which were provided with a thin insulating coating and which had a mean particle size above 212 µm was surface modified with 0.1 % and 0.2 % of hexadecyl trimethoxysilane, respectively, according to the procedure in example 1. The same iron- based powder without any surface modifying agent was used as a reference.

Cylindrical samples with a diameter of 25 mm and a height of 4 mm were compacted in an uniaxial press movement at a compaction pressure of 1000 MPa.

Table 2 shows the ejection energy needed for ejecting the components and the green density obtained. The ejection energy is expressed as percentage of the ejection energy for the sample without surface modification.

Table 2

Amount of silane	Green density	Relative Ejection Energy	Surface finish
0 %	7.66 g/cm ³	100	Poor
0.1 %	7.67 g/cm ³	58	Good
0.2 %	7.66 g/cm ³	48	Good

From table 2 it can be seen that the energy needed for ejection is considerably reduced and the surface finish is improved by minor additions of a surface modifying agent. It can also be seen that an increase from 0.1 % to 0.2 % by weight of a surface modifying agent has a positive impact on the ejection energy.

Example 3

This example shows the effect of a different surface modifying agent, namely stearic acid compared with hexadecyl trimethoxysilane used in an amount of 0.2 % by weight of the composition to be compacted.

A high purity water atomised iron- based powder provided with a thin insulating coating with a mean particle size above 212 µm was surface modified with 0.2 % by weight of hexadecyl trimethoxysilane and 0.2 % stearic acid, respectively. The same surface modifying procedure for the hexadecyl trimethoxysilane as in example 1 was applied. For stearic acid the following surface modifying procedure was used:

The stearic acid was dissolved in acetone for the preparation of a 5 % by weight solution. An amount of this solution corresponding to 0.2 % of stearic acid was added to the iron- based powder mixture which has previously been heated to 45 °C, during mixing. An intensive mixing was carried out in the same mixer during 3 minutes followed by mixing at a lower speed during 30 minutes and during vacuum in order to evaporate the solvent. The obtained mixture was sieved on 500 µm sieve.

Cylindrical samples with a diameter of 25 mm and a height of 4 mm were compacted in an uniaxial press movement at a compaction pressure of 1000 MPa.

Table 3 shows the ejection energy needed for ejecting the components and the green density obtained. The ejection energy is expressed as percentage of the ejection energy for the sample with 0.2 % silane.

Table 3

Surface modifying agent	Green density	Relative Ejection Energy	Surface appearance
0.2 % silane	7.61 g/cm ³	100	Good surface finish
0.2 % stearic acid	7.58 g/cm ³	97	Good surface finish

As can be seen from table 3 high green densities, the same ejection energies and perfect surface finish were obtained with both hexadecyl trimethoxysilane and stearic acid as surface modifying agents.

Example 4

The influence of particle size and particle size distribution was further investigated in example 4.

Three different high purity iron- based powder with different particle size distribution, according to table 4, all of them insulated with a thin phosphate- based electrical insulation were prepared. All samples were surface modified with 0.2 % of hexadecyl trimethoxysilane according to the procedure described in example 1.

Cylindrical samples with a diameter of 25 mm and a weight of 50 grams were compacted in an uniaxial press movement at a compaction pressure of 1000 MPa and green densities above 7.6 g/cm³ for all the samples were obtained.

Table 4

Particle size distribution %	Sample A	Sample B	Sample C
-45 µm	8.4	0.0	0.1
45-106 µm	52.7	15.5	1.0
106-212 µm	30.0	84.3	37.4
212-315 µm	0.1	0.2	51.0
+315 µm	0.1	0.0	10.5

Figure 2 shows the surface finish of the samples. As can be seen from this figure a significant amount of scratches are present on the surface of sample A, a less amount on the surface of sample B and an insignificant amount of scratches on the surface of sample C.

CLAIMS

1. A ferromagnetic powder essentially consisting of soft magnetic iron-based core particles wherein the surfaces of the core particles are surrounded by a first, electrically insulating coating and wherein a second coating of a surface modifying agent is present on the insulating coating.
2. Powder according to claim 1, wherein the surface-modifying agent is selected from the group consisting of surface modifying agent, which may be selected from the group consisting of organo alkoxysilanes, organo silazanes, fluorine-containing silicon silane coupling agents, titanate coupling agents, Zr and Al coupling agents, fatty acids, fatty acid esters, fatty acid amides, mixed fatty acid amides, fatty acid derivative mixtures and metal soaps.
3. Powder according to claim 2, wherein the surface-modifying agent is selected from alkylalkoxy silanes or alkylsilazanes, wherein the alkyl group has between 10- 24 carbon atoms, and fatty acids with 11-25 carbon atoms.
4. Powder according to claim 3, wherein the surface-modifying agent is hexadecyl trimethoxysilane .
5. Powder according to claim 2, wherein the surface-modifying agent is stearic acid.
6. Powder according to any of claims 1-5, wherein the surface modifying agent is present in an amount of 0.005- 0.5 %, preferably between 0.01- 0.4 % and most preferably between 0.05- 0.3 % by weight.
7. Powder according to any of claims 1-6, wherein the electrically insulating layer surrounding the iron or iron-based particles is made up of an inorganic material.
8. Powder according to claim 1-7, wherein the inorganic electrically insulating layer surrounding the iron- based particles is phosphorous based.
9. Powder according to any of claim 1-8, wherein the iron-based powder is an essentially pure iron powder.

10. Powder according to any of claim 1-9, wherein the iron-based powder has irregularly shaped particles.

11. Powder according to any of claim 1-10, wherein the iron-based powder is selected from the group consisting of water atomised powders and sponge iron powders.

12. Powder according any one of claim 1-11, wherein less than about 5 % of the powder particles have a size below 45 µm.

13. Powder according to claim 12, wherein at least 10 %, preferably at least 40 % and most preferably at least 60 % of the iron-based powder consists of particles having a particle size above about 106 µm.

14. Powder according to the claim 13, wherein at least 10 %, preferably at least 40 % and most preferably at least 60 % of the iron-based powder consists of particles having a particle size above about 212 µm.

15. Process for the preparation of soft magnetic composite materials comprising the following steps:

- providing an iron-based powder, the particles of which are electrically insulated and subsequently modified with a surface-modifying agent and which powder is essentially free from fine particles;
- optionally mixing said powder with an additive;
- uniaxially compacting the obtained powder in a die at a compaction pressure of at least about 600 MPa; and
- ejecting the green body and
- optionally heat treating the compacted body.

16. Process according to claim 15, wherein the compaction is performed at a pressure of at least 600 MPa, more preferably at least 800 and most preferably above 1000 MPa.

17. Process according to any one of the claims 15-16, wherein the compaction is performed at ambient temperature.

18. Process according to any one of the claims 15-17, wherein the compaction is performed at elevated temperature.

19. Process according to any one of the claims 15-17, wherein the compacted body is heat treated.

ABSTRACT

The present invention concerns a new ferromagnetic powder essentially consisting of soft magnetic iron-based core particles wherein the surfaces of the core particles are surrounded by a first, electrically insulating coating and wherein a second coating of a surface modifying agent is present on the insulating coating. The invention also concerns a process for the preparation of high density, high strength soft magnetic composite parts by compacting the new powder at high compaction pressures.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
13

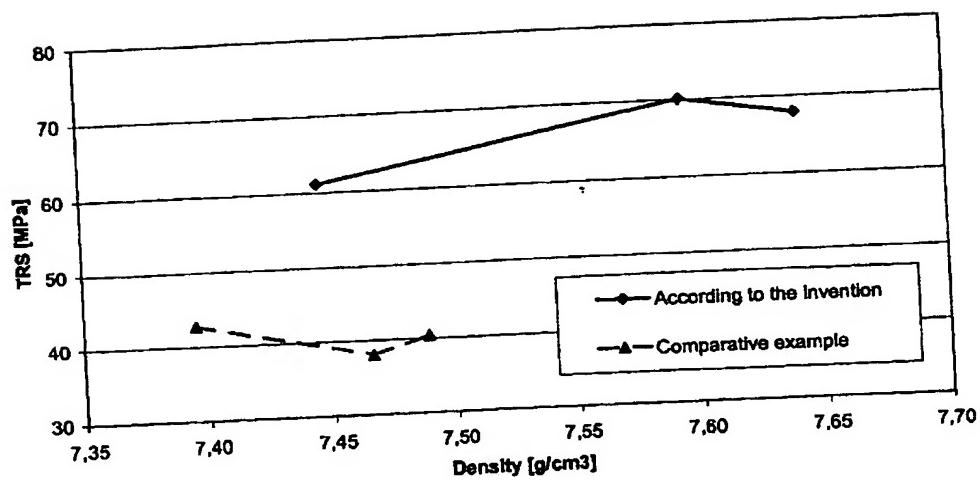


Figure 1

4000 000 000 000

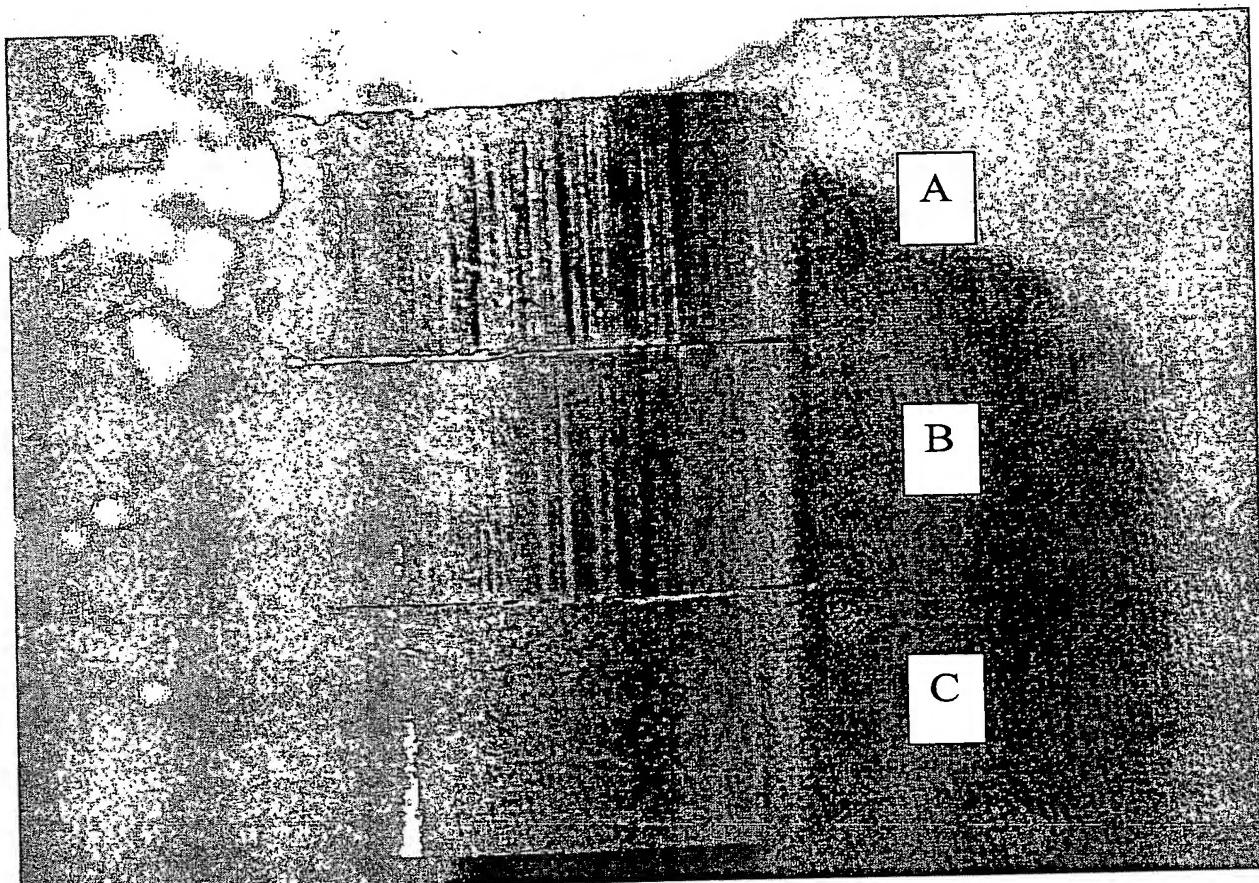


Figure 2